Towards Comprehensive Hydrocarbons Analysis of Middle Distillates by LC–GCxGC

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Abstract

The detailed characterization of middle distillates is essential for a better understanding of reactions involved in refining processes. Owing to a higher resolution power and an enhanced sensitivity, but especially to a group-type ordering in the chromatographic plane, comprehensive two-dimensional gas chromatography (GCxGC) offers unsurpassed characterization possibilities for petroleum samples. However, GCxGC fails to totally discriminate naphthenes from unsaturates occurring in hydrotreated diesel samples. This article aims at promoting the implementation of LC–GCxGC for the quantitative determination of hydrocarbon distribution in middle distillates, including naphthenes. In this configuration, liquid chromatography (LC) enables the separation of hydrocarbons into two fractions (viz., saturated and unsaturated) before the subsequent analysis of each fraction by GCxGC. In this paper, the choice of GCxGC conditions in order to achieve the separation and identification of hydrocarbons by chemical class is discussed; under these conditions, naphthenes are separated according to the number of saturated rings. For the first time, the presence of di-, tri-, and tetra-naphthenes resulting from the hydroconversion of aromatics can clearly be evidenced. A quantitative procedure for the determination of the distribution of hydrocarbons, including the distribution of naphthenes according to the number of saturated rings, is also proposed and discussed in detail. LC–GCxGC is found to provide an unequalled degree of information that will widely contribute to a better understanding of hydroconversion processes.

Introduction

Because of the growing demand for fossil fuels, there is a strong need to unravel the composition of petroleum streams or processed samples. Indeed, the detailed molecular characterization of a feedstock and the resulting products is a critical issue for the better understanding and improvement of hydroconversion processes. For example, it is known that the reactivity of hydrocarbons depends on the chemical class and the alkylation grade (which corresponds to the total number of carbon atoms) (1). Consequently, the distribution of hydrocarbons by family and by carbon breakdown is a key piece of information for building more accurate kinetic and thermodynamic models used for the optimization of refining processes (2).

Among available analytical methods, mass spectrometry (MS) has become the reference method. One MS method (ASTM D-2425) devoted to middle distillates has been normalized to determine the distribution of twelve hydrocarbon families, including two families of sulfur compounds. However, this technique strongly depends on the matrix of the sample to be analyzed, and calibration is required. Chromatographic methods, gas chromatography (GC) in particular, allow the separation of analytes according to their volatility. However, the complexity of the oil cuts increases exponentially with the boiling points (bp), and comprehensive separation in GC is limited to gasoline (3); that is, products having boiling points lower than 150°C.

In order to increase peak capacity, systems which are based on the association of several chromatographic techniques (the multidimensional systems) have been introduced. In the last decade, comprehensive two-dimensional gas chromatography (GCxGC) has been shown to be a very powerful tool for unraveling complex mixtures (4). Many studies underline the benefits of GCxGC in terms of peak capacity (5,6) and sensitivity (7,8), especially for the characterization of gasoline (9), kerosene (10), and diesel cuts (11), as well as for the control of petrochemical processes (Fisher Tropsch, oligomerization of olefins, etc.) (12).

Despite its high peak capacity, GCxGC still lacks the selectivity to fully resolve all families of hydrocarbons in middle distillates when conventional column association is used; in other words, the dimensionality of middle distillates is far greater than that of GCxGC, so that one or more analysis dimensions are needed (13). More generally, the lack of selectivity of GC columns prevents the correct separation of paraffins, naphthenes, and olefins (14).

A possible way to improve the selectivity in GCxGC consists of the implementation of an additional separation dimension. From this point of view, adding a pre-separation step such as GC, adsorption, normal-phase liquid chromatography (LC), or supercritical fluid chromatography theoretically offers the possibility of stacking complementary retention mechanisms (15,16) to separate analytes according to their chemical class prior to GCxGC analysis.

Thus, using GC as fractionation step, Vendeuvre (14) proposed...
the hyphenation of a silver (I) impregnated silica trap which selectively builds complexes with unsaturated hydrocarbons (17) and allows the sequential analysis of saturated and unsaturated hydrocarbons using GC×GC. However, this approach is limited to heavy naphtha cuts (C8–C15): it was shown that heavier compounds cannot be desorbed from the trap without being cracked.

Therefore, for heavier products, Edam et al. (13) recently proposed an approach based on offline LC fractionation. Using an amionopropyl LC column which separates hydrocarbons according to the number of aromatic rings, this group demonstrated that when GC×GC is carried out, the retention of triphenethenes is equivalent to the retention of monoaromatics in the second dimension on the two-dimensional GC×GC chromatographic plane. Thus it was shown that when polycyclic naphthenes occur, as is the case for hydrotreated diesel samples, the PIONA (Paraffins, Isoparaffins, Olefins, Naphthenes, and Aromatics) analysis cannot be achieved in GC×GC unless prior fractionation is conducted. Unfortunately, in this work, no individual identification could be achieved and LC effluent’s sampling at 0.2 Hz resulted in a large amount of fractions, which prevented any quantitative study of polycyclic naphthenes in diesel samples.

In order to improve the detailed PIONA analysis of representative middle distillates from various origins and processes, a quantitative multidimensional approach based on the offline hyphenation of adsorption LC with GC×GC is proposed in this work. First, this approach was applied to the identification of saturated and unsaturated compounds. In the second part of this study, a quantitation procedure of saturated and unsaturated hydrocarbons, including naphthenes and coeluting aromatics, is discussed. The last part of this paper is dedicated to the application of this quantitative procedure to deeply hydrotreated diesel samples.

Experimental

Preparative LC fractionation

Separation of saturated and unsaturated fractions was performed using preparative adsorption LC. The LC system was equipped with a preparative column (110 × 7.75-cm i.d.) which was filled with a mix (25:35 w/w) of neat silica (100–200 mesh) and gamma-alumina (70–230 mesh) supplied by Merck (Darmstadt, Germany). After conditioning for 30 min under n-heptane flow, the sample (2.0 g) diluted in n-heptane was injected via a 4 mL injection loop. The group-type separation was performed at room temperature using a mobile phase program consisting of n-heptane (0–37 min, elution of the saturated fraction) and a mix of n-heptane and dichloromethane (37–217 min, elution of the unsaturated fraction). The mobile phase was delivered by a pump (Model 510, Waters, Guyancourt, France) at a constant flow of 2 mL/min. The saturated (84 mL) and unsaturated (320 mL) fractions were isolated based on retention times measured for real diesel samples using a refractometer (model 2414, Waters, Guyancourt, France). To prevent sample loss, no evaporation of fractions was carried out prior to GC×GC analysis.

The ability of the LC procedure to separate saturated and unsaturated hydrocarbons by an adsorption mechanism has been investigated. For that purpose, real samples containing all hydrocarbon types were separated into saturated and unsaturated fractions using the preparative LC procedure as described previously. Afterwards, collected fractions were subjected to a mass spectrometry (MS) analysis, which confirmed the absence of saturated and unsaturated compounds in the unsaturated and saturated fractions, respectively, indicating that a full separation of both classes of compounds could be achieved under selected LC conditions. Based on five replicates, the LC method was found to be repeatable and selective (recovery yields ranged between 99% and 100%), indicating the excellent ability of the LC procedure to quantitatively handle both saturated and unsaturated compounds separately.

GC×GC–FID

The GC×GC system consisted of a modified standard GC HP 6890N (Agilent Technologies, Massy, France). The modulator was a dual stage carbon dioxide jet modulator built in-house as described by Beens (18). Modulation was set at 12 s. In this work, the GC×GC analysis was carried out first with a nonpolar column (PONA, dimethylylpolysiloxane, Agilent Technologies, 15 m × 0.2 mm × 0.5 µm). The impact of the nature of different stationary phases in the second dimension (BPX 50 [50% phenyl]-polysilphenylen-siloxane [SGE, Courtaboeuf, France] and β-Dex 120 [20% permethylated β-cyclodextrin in a SPB 35 matrix] Supelco, Lyon, France) was studied and discussed with the results in the “Qualitative study of diesel samples” section. The separation was carried out at a constant flow of 0.9 mL/min. A flame ionization detector (FID) set at 320°C was used for detection: H2, air, and He (make up) flows were 35, 400, and 25 mL/min, respectively. Oven temperature was increased from 50°C to 300°C at a rate of 2°C/min. Respectively, 1 and 2 µL of the saturated and unsaturated fractions were injected in splitless mode using an auto sampler (Model 7683, Agilent Technologies) equipped with a 5 µL syringe. The concentration of the injected fraction depends on the non aromatics/aromatics ratio of the diesel being considered. It was found to be in the 7.9–21.1 mg/mL and 2.2–5.6 mg/mL ranges for non-aromatics and aromatics, respectively. After acquisition, the signal was exported as a CSV-file from the Chemstation for data handling. Contour plotting, GC×GC peak collection, retention time measurements, peak integration, and report were done using an in-house software named Polychrom, featuring automatic peak finding and blob fitting in order to improve reproducibility and accuracy of integration. Intensities are indicated by means of a colour contrast ranging from pale blue to dark blue for minor and major peaks, respectively.

GC×GC–TOF–MS

For identification purposes, a LECO Pegasus IV (LECO Corporation, St Joseph, MI) GC×GC–time-of-flight (TOF)–MS system was used. The HP 6890 chromatograph was equipped with a “Split” injector (Agilent Technologies) and a liquid nitrogen cooled gas jet cryogenic modulator. Electron impact ionization was performed at 70 eV, the acquisition frequency was set at 100 Hz in a mass range of 35 to 500 amu, and a multi-plate voltage of −1450 V was applied. Chromatograph and detector
control, data collection, and processing were performed using the Chroma TOF software. Identification of molecules was carried out by comparison of the acquired spectra with the NIST 2.0 (2002) spectra database. Other operating conditions (columns, carrier gas, flow, oven program, etc.) were analogous to those used for the GC×GC–FID system.

**GC Simulated Distillation**

Simulated distillation (SimDis) analysis was achieved using an HP 5890 chromatograph (Agilent Technologies) equipped with an FID and a cool on-column inlet. Analysis was carried out at a constant helium flow of 10 mL/min on a MXT-1 (Restek, France) Silcosteel-treated stainless steel capillary column (15 m × 0.53 mm × 0.5 µm) which was heated from 35°C (hold 1 minute) to 390°C at a rate of 10°C/min. Detector temperature was set at 400°C. The SimDis curve was obtained by using the algorithm defined in the ASTM D-2887 method. Calculation was performed using the Chromdis software (Gecil Process, France).

**Samples**

Diesel cuts were provided by IFP-Lyon and were obtained from direct atmospheric distillation of crude oils (referred to as straight run [SR] diesel), from cracking processes (referred to as Light Cycle Oil [LCO] or Hydroconversion [HDK] diesel samples), or from the hydrotreatment process (referred to as HDT diesel sample). The properties of the diesel samples used in this work are presented in Table I. For details regarding petrochemical processes, reader is referred to the literature (19).

**Fluids**

Analytical gases were provided by Air Liquide (Feyzin, France) at a minimum purity of 99.999%. LC solvents of HPLC grade were purchased from Sigma-Aldrich (St Quentin Fallavier, France).

**Results**

**Qualitative study of diesel samples**

The goal of this paper is the identification and quantitation of saturated compounds generally coeluting with monoaromatics in GC×GC. Therefore, in this work, a nonpolar/polar column association was preferred to a polar/nonpolar approach, which offers less benefit from a quantitative point of view, especially when the distribution of hydrocarbons according to the number of carbon atoms within each chemically related class of hydrocarbon has to be determined (20). Such an approach usually occurs first in a nonpolar column (PONA) which first allows a separation according to the volatility of compounds and a short second polar column consisting of polysilphenylenesiloxane (BPX 50), separating compounds according to the number of aromatic rings. In addition, a secondary column likely to discriminate hydrocarbons according to the shape of analytes, a β-cyclodextrine column, was studied.

The two-dimensional chromatogram of a deeply hydrotreated diesel sample (diesel sample A) obtained using a PONA primary column and a BPX 50 secondary column is presented in Figure 1 (See page 6A) and clearly shows that under these chromatographic conditions, the separation of saturated and unsaturated compounds is not satisfactory. Indeed, naphthenes and aromatics are eluted according to their polarity (i.e., according to the number of rings) (20). Consequently, retention times increase according to the second separation dimension (BPX 50), leading to a coelution, starting as early as 30 min, of tri- and tetra-naphthenes with monoaromatics and naphthenic monoaromatics, respectively (coelutions zone is shown in Figure 1 (see page 6A). For instance, at a given first dimension retention time of 60 min (oven temperature 170°C), trinaphthenes, tetrinaphthenes, monoaromatics, and naphthenic monoaromatics elute at 5.8, 6.2, 5.2, and 6.0 s respectively.

To overcome these coelutions, the ability of shape selective columns (β-Dex 120 column) was evaluated in the second dimension. For that purpose, the resolution (Rs) according to the second dimension between model compounds eluting at about the same temperature from the first column was evaluated. Ideally, to evaluate the ability of the shape selective column to resolve the issue of coeluting compounds, resolution should have been evaluated using monoaromatics and trinaphthenes as test compounds; however, because these compounds were not commercially available, alkyl monoaromatics and alkyl mononaphthenes were used. It was assumed that if the separation of these late compounds would have been improved, separation of trinaphthenic compounds and alkylmonoaromatics would also have been improved. In this respect, Rs between n-alkyl mononaphthenes and the n-alkyl monoaromatics having one atom of carbon more than the considered naphthenede was considered (corresponding normal paraffins [noted CX, where X corresponds to the number of carbon atoms] are specified in Figure 2). To allow the comparison of resolution values, both secondary columns (BPX 50 or β-dex 120, 1.0 m × 0.1 mm × 0.1 µm) were successively operated with the same first dimension column (PONA, 15 m × 0.2 mm × 0.5 µm) under the same operating conditions as mentioned in the “GC×GC–FID” section. The resolution values measured according to the second dimension are compared within a 5% confidence interval in Figure 2.

| Table I. Properties of Diesel Samples Studied |
|-------------------------------|----------------|----------------|----------------|----------------|----------------|
|                               | Diesel A        | Diesel B        | Diesel C        | Diesel D        | Diesel E        |
| Density at 15°C (g/cm³)*      | 0.8737          | 0.9366          | 0.8535          | 0.8752          | 0.9415          |
| Total sulfur (% S)            | 0.00            | 1.80            | 0.07            | 0.46            | 1.53            |
| non aromatics/ aromatics ratio (% w/w)‡ | 65/34          | 27/73           | 63/37           | 71/29           | 28/72           |

* ASTM D-4052 Density and Relative Density of Liquids by Digital Density Meter.
† ASTM D-2887-03 Simulated distillation method (5–95% weight).
‡ When occurring, olefins were quantitated with non-aromatic compounds.
Resolution obtained on β-Dex 120 is nearly identical to the resolution observed on BPX 50 and almost constant, with an average of 2.9, despite better separation of peak apexes. This is related to differences in apparent efficiency, as peak width is larger (ca. 1.4 times) on β-Dex 120 than on BPX 50, indicating that compared to conventional BPX 50 stationary phase, shape selective secondary column does not improve the selectivity towards naphthenes and monoaromatics.

Among the various stationary phases tested, no evidence of selectivity and separation improvement using a very short second dimension column was found; therefore, the implementation of an additional separation dimension prior to GC×GC analysis was investigated to provide improved separation of polyaromatics and naphthenes.

To cyclic naphthenes from monoaromatics. Because it enables group-type separation, adsorption LC separation was chosen. To increase the peak capacity and achieve a better occupation of the two-dimensional plane, GC×GC chromatographic conditions were adapted and a longer (2.1 m × 0.1 mm × 0.1 µm) secondary column was preferred to conventional secondary columns (1.0 m × 0.1 mm × 0.1 µm) (21).

Figure 3 (See page 6A) presents the two-dimensional chromatograms of the saturated (Figure 3A, See page 6A) and unsaturated (Figure 3B) fractions obtained for diesel sample A. Structures of compounds occurring in both the saturated and unsaturated fractions have been identified using the GC×GC–TOF–MS system. In order to get rid of wrapping around occurring on naphthenics, diaromatics, and triaromatics, and to facilitate comparison of chromatograms, a 3 s offset was applied according to this dimension on Figure 3B (see page 6A); therefore, to allow the comparison of the two fractions, the band corresponding to monoaromatics has been drawn on the two-dimensional chromatograms with a dashed line. Comparison of the two-dimensional chromatograms obtained for the saturated and unsaturated fractions confirms that saturated compounds are coeluted with monoaromatics. As expected from the literature (20), aromatics are structured according to the number of aromatic rings, and a distinction can even be made between naphthenic aromatics and condensed aromatics. The chromatogram of the saturated fraction (Figure 3A, see page 6A) reveals that apart from being separated according to the number of naphthenic rings, each band of naphthenics is divided into sub-bands corresponding to groups of molecules having the same number of carbon atoms. As an illustration, a zoom of saturated fraction is presented in Figure 3C (see page 6A) and typical structures, identified using GC×GC–TOF–MS, are reported. One should note that owing to the presence of asymmetric carbons, several isomers are likely to occur in petroleum samples. For instance, decaline (molecule #2, Figure 3C, see page 6A) has two asymmetric carbons resulting in the presence of two diastereoisomers (RR or RS). In this case, GC×GC succeeds in separating these two molecules, but the MS detector fails to correctly distinguish both isomers. As the first separation is achieved on a nonpolar column (PONA), it only discriminates analytes according to their volatility (or boiling points). Therefore, under these operating conditions, the first and the second decaline peaks could be attributed to trans-decaline (bp: 185°C) and cis-decaline (bp: 193°C), respectively. For heavier molecules, the number of isomers increases significantly; nevertheless, the same approach can be adopted to distinguish the different isomers.

In the case of diesel samples containing olefins, such as LCO diesels (samples B and E), olefins appear on the chromatograms of the unsaturated fraction. Their chromatographic behavior is nearly the same as the paraffinic mononaphthenic hydrocarbons (i.e., they would hardly be separated without prior LC fractionation).

Validation of the quantitation procedure
The LC–GC×GC–FID separation described above was used in order to determine the relative contents of the different classes of hydrocarbons present in each diesel. In order to compare the LC–GC×GC approach with GC×GC, a LCO (diesel B) was selected as the test sample because MS data shows that it does not contain polynaphthenic hydrocar-

<table>
<thead>
<tr>
<th>Description</th>
<th>GC×GC analysis with fractionation (% w/w)</th>
<th>GC×GC analysis without fractionation (% w/w)</th>
<th>Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffins</td>
<td>20.2 ± 2.4</td>
<td>20.4 ± 2.4</td>
<td>NS</td>
</tr>
<tr>
<td>Naphthenes</td>
<td>7.5 ± 0.9</td>
<td>7.0 ± 0.8</td>
<td>NS</td>
</tr>
<tr>
<td>Monoaromatics</td>
<td>20.1 ± 2.4</td>
<td>20.5 ± 2.4</td>
<td>NS</td>
</tr>
<tr>
<td>Diaromatics</td>
<td>41.0 ± 4.9</td>
<td>42.3 ± 5.1</td>
<td>NS</td>
</tr>
<tr>
<td>Triaromatics</td>
<td>11.2 ± 1.3</td>
<td>9.8 ± 1.2</td>
<td>NS</td>
</tr>
</tbody>
</table>
bons likely to coelute with aromatics in GC×GC as shown in Figure 1 (see page 6A). Thus, it was possible to quantitate the various chemical families without interferences in GC×GC.

**Description of the LC–GC×GC quantitation procedure**

To take into account the discrimination at both injection and detection, specific response factors were determined using a mixture containing all normal paraffins in the C12–C24 range. Then, the area was converted in a weight percent using the response factors, and the content of each group in its respective fraction of origin was determined. For the two LC–GC×GC fractions, it was necessary to use a corrective factor ($f_{ci}$, equation 1) defined as the ratio of the injected volume ($V_{inj,i}$) of fraction i (saturated or unsaturated) to the volume of the considered fraction ($V_i$): for instance, the content of family j in the full diesel sample ($C_{ij}$) was obtained from the content of family j initially present in fraction i ($C_{ij,i}$), using equation 2. One should note that equation 1 (and equation 2) refer to different volumes used for the saturated and non-saturated fractions. Indeed, because dilution volumes differ from one fraction to the other, different injection volumes were required to be within detectability limits of GC×GC analyses.

$$f_{ci} = \frac{V_{inj,i}}{V_i} \quad \text{Eq. 1}$$

$$C_j = f_{ci} \times C_{ij} \quad \text{Eq. 2}$$

**Evaluation of the LC–GC×GC quantitation procedure**

Table II presents the results obtained with and without the fractionation procedure (for both procedures, relative standard deviation [RSD] is 12%, based on five replicates with a 99% confidence) for diesel B. For this evaluation, no distinction between the different types of naphthenes was considered. Results show that the differences observed between the values obtained with and without the fractionation step for each class of compounds are non-significant, indicating that there is no bias when LC is carried out as a fractionation step prior to GC×GC.

**Impact of the fractionation step on the hydrocarbon distribution**

Additionally, in order to make sure that the fractionation procedure did not give rise to a modification of the distribution of hydrocarbons, particularly at the expense of volatile compounds, the simulated distillation curves obtained for diesel B with and without fractionation were compared.

Simulated distillation curves of the fractionated diesel sample were obtained from the two-dimensional chromatograms of each LC fraction. Using the data obtained for the quantitation of each chemical group, the elution zone was divided into slices of which depends on the percentage of hydrocarbons having a bp above 350°C. Indeed, when the percentage of hydrocarbons having a bp above 350°C exceeds 20% w/w, which is the case of diesel samples A and D, the LC–GC×GC approach seems to overestimate paraffins at the expense of naphthenes and diaromatics. As it was shown in the “Validation” section, neither the fractionation nor the integration procedure is responsible for this bias, but one could question the MS method (ASTM D-2425 method), the reliability of which depends on the percentage of hydrocarbons having a bp above 350°C. Indeed, when the percentage of hydrocarbons having a bp above 350°C exceeds 20% w/w, which is the case of diesel samples A and D, results are known to be biased. In this case, the yields of ionization of the heaviest products are weaker than those of the light products, which results in a bias; in other words, MS methods underestimate saturates at the expense of aromatics.

Based on these results, the LC–GC×GC approach offers the possibility of achieving a deeper insight into diesel samples, especially if one considers that the distribution of naphthenes according to the number of rings as well as the number of atoms of carbons can be reached. Furthermore, compared to the MS...
method (ASTM D-2425), the LC–GCxGC approach is more accurate and matrix independent, therefore it was applied to the study of the hydrotreatment of a LCO diesel.

**Application of the LC–GCxGC procedure to the study of the hydroconversion of a diesel sample**

Based on the procedure proposed in this work, it becomes possible to better understand hydrodearomatization (HDA) pathways; it is now widely accepted that HDA involves direct hydrogenolysis (ring opening) and hydrogenation (double bond hydrogenation), and it is also well known that these two pathways are slightly different. For instance, hydrogenolysis cannot take place directly and hydrogenation has to occur before hydrogenolysis can take place (22). Thus, the knowledge of detailed molecular composition can allow the identification of refractory compounds as well as the preferred route for the process, which is of major importance for a careful monitoring of refining plants.

To illustrate the powerful capabilities of this new approach, LC–GCxGC was applied to the study of a conversion process (hydrotreatment). For that purpose, quantitative repartition of hydrocarbons, including the distribution of naphthenes according to the number of saturated rings, in a feedstock (diesel E) and the corresponding hydrotreated product (diesel A) was determined using the LC–GCxGC approach. In this case, olefins, which were recovered in the aromatic fraction, were also quantified by LC–GCxGC. Sulfur compounds which occurred exclusively in the form of benzothiophenes and dibenzothiophenes (DBT) were taken into account separately and determined by mass spectrometry according to method ASTM D-2425. Raw data are reported in Table IV and a balance sheet based on the number of cycles of hydrocarbons in the feedstock and the product is drawn up in Figure 5 (see page 6A).

The presence in the product of four ring compounds (tetraaromatics) can only result from the hydrotreatment of tetraaromatics or naphthenic triaromatics initially present in the feedstock. The relative concentrations (shown in Figure 5, see page 6A) indicate a total conversion of tetraaromatics and naphthenic triaromatics into tetranaphthenes exclusively by hydrogenation. For tricyclic compounds, the same conclusions could be drawn. Indeed, because tetraaromatics were fully transformed into tetranaphthenes, tricyclic hydrocarbons in the product (triaromatics, naphthenic diaromatics, triaromatics) can only result from the hydrogenation of triaromatics and naphthenic diaromatics occurring in the feedstock. In addition, Figure 5 (see page 6A) shows that the global content of tricyclic compounds in the feed roughly corresponds to the amount of tricyclic compounds present in the feed, indicating that no ring opening occurred (i.e., that hydrogenation pathway was preferred to hydrogenolysis in this case). One should also note that the conversion of triaromatics is partial, indicating that hydrogenation kinetics are less favourable to triaromatics than to tetraaromatics, which were totally removed by hydrotreatment.

In the case of dicyclic compounds, the conversion of diaromatics and naphthenic monoaaromatics as well as of sulfur compounds likely to yield dinaphthenes (in this case, the dibenzothiophenes) has to be considered. Results reported in Figure 5 (see page 6A) indicate that hydrogenation is the favorite route for hydrocarbons. Regarding sulfur compounds, the balance shown in Figure 5 (see page 6A) seems to demonstrate that most of DBT were totally hydrogenolized (opening of the thiophenic cycle) and hydrogenated (aromatic rings) to yield non-condensed dinaphthenes, which coeluted with condensed dinaphthenes under the selected operating conditions.

The study of the conversion of monocyclic compounds also demonstrates that hydrogenation is the favorite route for hydrocarbons, whereas sulfur compounds likely to be transformed into one ring compounds (in this case,
the benzothiophenes) are hydrogenolized and hydrogenated to exclusively yield mononaphthenes. For further details regarding the conversion of sulfur compounds, GC×GC–sulfur-chemiluminescence detector analysis, as proposed by Ruiz-Guerrero (23), would be desirable.

In the case of non-cyclic compounds, the increase of paraffin content could be related to the total hydrogenation of olefins occurring in the feed.

These results demonstrate that in the case of the studied diesel sample, hydrogenation was the favorite hydrotreatment route. These results also underline the benefits of the LC–GC procedure, which allows for the first time a comprehensive study of the hydroconversion of real samples.

Conclusion

In this paper, a new approach based on a three-dimensional chromatographic system was proposed. For the first time, di-, tri-, and tetra-naphthenic hydrocarbons, resulting from the hydrotreatment of di-, tri-, and tetra-aromatics, could be unequivocally identified by TOF–MS coupled to LC–GC.

The proposed quantitation procedure was evaluated, discussed, and applied to the study of the hydroconversion of a diesel sample: the LC–GC approach advantageously offers the possibility (i) to evidence products formed during conversion process and (ii) to determine the conversion pathways, which is undoubtedly of major importance for kinetic and thermodynamic models used to monitor refining plants.

Further work is now needed to miniaturize and truly hyphenate the fractionation step to the GC×GC system for routine analysis.

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References


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